

PYRIDINE SORPTION BY PYRIDINE-EXTRACT
OF ILLINOIS NO. 6 COAL

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KEYWORDS: Coal swelling, Extracts, Pyridine

INTRODUCTION

The principal goal of this research is to develop an understanding of the thermodynamics of the swelling of coals in various solvents. The approach is unique in the sense that the uncrosslinked portion of the coal is being swollen, as opposed to the crosslinked portion. This approach avoids complications due to the crosslinked nature of coals, and allows the experimental data to be interpreted in terms of modern theories developed for polymer solutions.¹

The uncrosslinked portion of the coal is obtained by pyridine-extraction of the coal. The extract is then swollen with the solvent at several relative pressures until equilibrium is established. In principle, free energies, enthalpies, and entropies of swelling can be determined from such an approach.

We are currently working with the pyridine-extract of an Argonne premium Illinois No. 6 coal. This coal is about 27% (wt) Soxhlet extractable in pyridine. The carbon, hydrogen and nitrogen contents of the extract are very similar to those of the original coal. The extract was exposed to pyridine at several relative pressures and the equilibrium weight of pyridine was measured. Studies were conducted at both 50°C and 70°C. We also studied the O-methylated extract under the same conditions.

EXPERIMENTAL

Sample preparation. Argonne Premium Illinois No. 6 coal was obtained from Argonne National Laboratory in ampoules of five grams of -100 mesh coal. The coal was first dried under vacuum at 105°C to constant weight and then analyzed for carbon, hydrogen, and nitrogen. Analysis found: C, 65.57; H, 4.66; N, 1.24 (duplicate).

Approximately 4.5 g of the sample was Soxhlet-extracted with dry pyridine under argon for several days until the siphon liquid was clear. The pyridine solution was then filtered through a 0.4 μ m nylon membrane filter to insure removal of particulates and colloidal material. The filter did not plug. Most of the pyridine was removed by rotovaporization under reduced pressure at 70-80°C. Approximately 200 mL of a methanol/water (80/20 vol.) mixture and 2 mL of conc. HCl were added to the flask and the mixture was stirred under nitrogen for two days. The solid extract was then filtered and dried under vacuum at 105°C for 24 hours. The extractability was 27.2% (wt.). This value agrees well with that found by Buchanan et al.² Analysis found: C, 78.32; H, 5.62; N, 1.65 (duplicate).

The pyridine-insoluble residue obtained from the extraction was first dried under vacuum to remove most of the pyridine, treated with the methanol/water/HCl mixture, and then dried under vacuum. Analysis found: C, 60.47; H, 4.39; N, 1.30 (duplicate).

The extract was O-methylated according to the procedure of Liotta.³ FT-IR analysis and carbon and hydrogen analysis confirmed that reaction had occurred. Analysis found: C, 76.7; H, 6.04; N, 1.24.

Sorption Experiments. Sorption experiments using pyridine as solvent were carried out using a quartz spring balance shown in Figure 1. The balance consists of a quartz spring, a large 5 liter flask, vacuum inlet system, and MKS pressure transducer (0-1000 torr, 0.5% accuracy). The entire balance chamber, including transducer, is housed in a Precision Scientific circulating (forced air) drying oven, which is maintained at a constant temperature by a I²R thermowatch temperature regulator which activates a light bulb.

The sample is suspended from the quartz spring and, as the sample sorbs solvent, the spring extends until equilibrium is reached. The extension of the spring is measured through a window on the door of the oven using a sensitive Eberbach cathetometer (travelling telescope). The spring is calibrated at the appropriate temperature using standard weights before the experiment is conducted. The experiment thus allows determination of the mass of solvent sorbed by the sample at a given partial pressure and temperature. The purpose of the 5 liter flask to minimize pressure changes caused by sorption of solvent by the sample. Quartz springs of the type used here have a linear-extension versus suspended-weight relationship and exhibit no hysteresis within the range of weights for which the spring is designed.

For the particular spring used in these experiments, the calibration factor was determined to be 0.48 mm/mg. The uncertainty of the cathetometer is ± 0.1 mm. Since two measurements must be made to obtain the weight of solvent, the uncertainty in the solvent weight is ± 0.2 mm \times 1 mg/0.48 mm = ± 0.4 mg. In a typical experiment, 50 mg of extract was used, so the uncertainty per gram of extract is ± 0.4 mg/0.050 g = ± 8 mg/g extract.

The experimental procedure was as follows. Approximately 50 mg of extract was placed in the quartz bucket and weighed on an electronic balance. The bucket and sample were then suspended on the spring. The hangdown tube was replaced and the system was evacuated to less than 0.1 torr and brought to the appropriate temperature. The system was allowed to evacuate overnight. Purified pyridine was placed in the round bottom flask shown in Figure 1 and frozen with dry ice/isopropanol. Stopcock B was closed, and stopcock C was opened to evacuate air from the flask. Then stopcock C was closed, and the pyridine was thawed and refrozen. Stopcock C was again reopened for evacuation. This procedure insures removal of last traces of air. Stopcock A was closed and stopcocks B and C were then opened until the appropriate pressure of pyridine was reached. After equilibrium was achieved, the pressure of pyridine was again raised. This procedure was repeated until the entire pressure range was covered.

RESULTS

Characterization of Pyridine Extract. Residual pyridine was removed from the pyridine-extract of the Argonne Illinois No. 6 coal by stirring with a methanol/water/HCl mixture for two days. Elemental analyses of the pyridine-extract revealed 1.65% N compared to 1.47% N (daf) in the original coal. The possibility exists that a small amount of pyridine remains bound to the extract. If one assumes that the additional N content of 0.18% is attributed to residual pyridine, then 10 mg pyridine/g extract was not removed from the extract by the methanol/water/HCl washing. FT-IR analysis failed to detect any residual pyridine, however.

The O-methylated extract was analyzed for carbon and hydrogen to establish the number of methyl groups added. The H/C ratio of the original extract is 0.86 and

the ratio of the O-methylated extract is 0.94. This increase in H/C ratio corresponds to the addition of 7.5 methyl groups per 100 carbon atoms of original extract. Liotta determined that there were approximately 5 acidic hydroxyl groups in an Illinois No. 6 coal,³ which is considerably lower than that determined here. However, our value is for the extract, not the whole coal, and it does not seem unreasonable. The O-methylated extract exhibited a reduced hydroxyl group absorption compared to the original extract, consistent with the conversion of phenolic hydroxyl groups to methyl ethers. In addition, a significant absorption at 1700 cm^{-1} appears in the spectrum of the O-methylated extract, consistent with the conversion of carboxylic acids to methyl esters.

Sorption Experiments. The pyridine-extract and O-methylated extract of the Argonne Illinois No. 6 coal were exposed to pyridine at various vapor pressures at 50°C and 70°C . Several incremental sorption experiments were conducted in that, once equilibrium was attained at a particular pressure, the pressure was raised, and the system was again allowed to attain equilibrium. Typical sorption curves for the extract and O-methylated extracts are shown in Figures 2 and 3, respectively. Note that a wide range of pressures was covered, ranging from 0.20 to 0.99. For the extract, several hours are required to reach equilibrium at each pressure and, in general, equilibrium was achieved more rapidly at the higher pressures. Equilibrium was achieved more rapidly for the O-methylated extract in comparison, particularly at the lower pressures.

The equilibrium amounts of pyridine determined from each sorption experiment are plotted against relative pressure of pyridine in Figure 4. Note that there is a good straight-line correlation between the sorption values and pressure for each extract and each temperature. The curves drawn are least-squares fits. The slope of the curve decreases upon O-methylation, i.e. the O-methylated extract sorbs less pyridine at equivalent relative pressures. Both extracts sorb less pyridine at the higher temperature.

DISCUSSION

The results in Figure 4 demonstrate that sorption of pyridine by the extract of the Illinois No. 6 coal obeys Henry's Law, i.e., the solubility of pyridine in the extract increases linearly with pressure. However, the curves do not pass through the origin. This result is similar to those of Michaels *et al.*, who observed that the solubilities of several gases in polyethylene terephthalate obeyed Henry's law.⁴ For two of the gases, carbon dioxide and ethane, the sorption isotherms were curved at low pressures but linear at higher pressures. They interpreted their results by proposing that sorption took place by two concurrent mechanisms at the lower pressures; ordinary dissolution and "hole-filling". At higher pressures, the holes or microvoids were saturated with only dissolution occurring. The intercept was interpreted as the total amount of sorption due to filling of the microvoids. Thus, a quantitative separation of the two processes was possible.

Following the work of Michaels *et al.*, we suggest that the intercepts observed in Figure 4 represent the total amount of pyridine that fills holes in the extracts. Using a density of 0.98 g/mL for pyridine, the total microvoid volume occupied by pyridine is determined to be 0.079 mL per g of extract (average of two values). Using a density of 1.3 g/mL for the extract (determined with helium), this corresponds to 9% microvoid volume for the extract. The same calculation for the O-methylated extract yields a value of 7% microvoid volume. Although caution is warranted at this time, we feel the magnitude of these values is reasonable.

Finally, we have corrected the sorption curves shown in Figure 4 for hole-filling according to the above model. The results are shown in Figure 5. These curves represent dissolution of pyridine into the extracts if our interpretation is

correct. We can calculate the differential heats of dilution for both the extract and the O-methylated extract from the data using Equation 1. The differential heat of dilution is defined as the heat change when one mole of pyridine is added to an infinite amount of the mixed phase at the specified concentration, and is given by

$$\Delta H_{dil} = -RT^2 \frac{d(\ln p/p_o)}{dT} \quad (1)$$

For the case in which solubility follows Henry's law, the heat of dilution is constant as a function of concentration, as long as the curves have the same intercept. Using an average temperature of 333 K, we calculate a ΔH_{dil} of -2.3 kcal/mole for the extract-pyridine system and a value of -4.5 kcal/mole for the O-methylated extract-pyridine system.

We feel the sign and magnitude of ΔH_{dil} calculated for the extract-pyridine system is reasonable, since pyridine is expected to hydrogen bond to phenolic groups in the extract, a process which is expected to be exothermic. Although the strength of hydrogen bonds between pyridine and phenols are typically on the order of 7 kcal/mole,³ it must be considered that coal-coal hydrogen bonds probably have to be broken in the extract in order to form a pyridine-coal hydrogen bond. (It is obvious in the IR spectrum of the extract that the hydroxyl groups in the extract must be hydrogen bonded). This process obviously costs energy, so the magnitude of ΔH_{dil} for this system is not unreasonable.

The more negative ΔH_{dil} for the O-methylated extract is surprising, particularly since hydrogen bonding is expected to be absent in this system. We currently have no explanation for this result. We simply suggest that perhaps there is a small population of sites in the O-methylated extract which interact strongly with pyridine. The nature of these sites is unknown, but they may be hydroxyl groups that were left unreacted by O-methylation. Clearly, more studies need to be done before conclusions can be drawn.

Finally, we note that the curves in Figure 4 indicate that there should be only limited swelling of the extracts at a relative pressure of 1.0. However, we have noted that both extracts can be substantially redissolved in liquid pyridine ($p/p_o=1.0$). Thus, it seems that the curves must rise very steeply as a relative pressure of 1.0 is approached. The data shown in Figure 4, however, do not support this idea. We presently have no explanation for this result.

CONCLUSIONS

Equilibrium sorption of pyridine by the pyridine-extract and the O-methylated extract of the Illinois No. 6 coal increases linearly with pressure. We tentatively interpret the intercept as the total amount of pyridine that fills microvoids in the extract. Equilibrium sorption of pyridine decreases with increasing temperature at equivalent relative pressures for both extracts, consistent with exothermic processes. We are currently conducting experiments on the whole coal to see if it might behave similarly. The results will be presented in the talk.

ACKNOWLEDGEMENTS

We gratefully acknowledge the Department of Energy, Grant No. DE-FG22-88PC88924, and the Research Corporation for support of this work.

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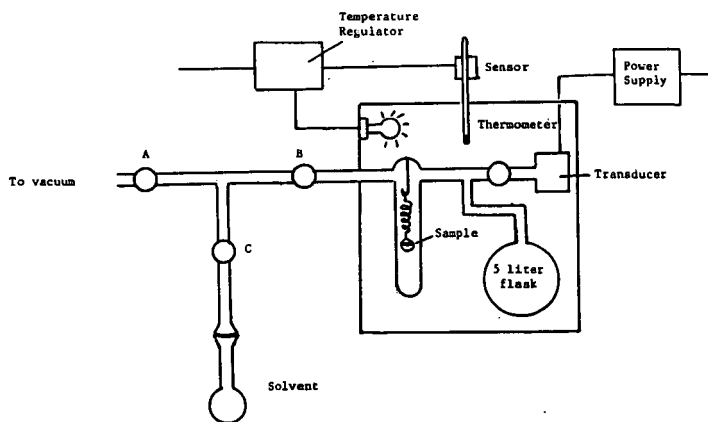


Figure 1. Sorption Apparatus

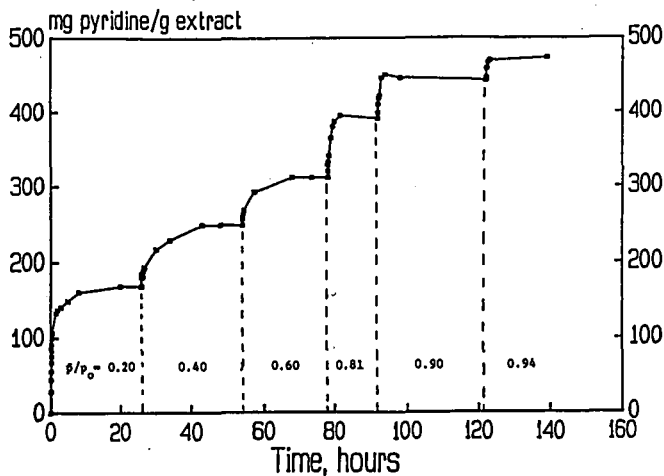


Figure 2. Sorption of Pyridine by Pyridine-extract of Illinois No. 6 Coal at 50°C.

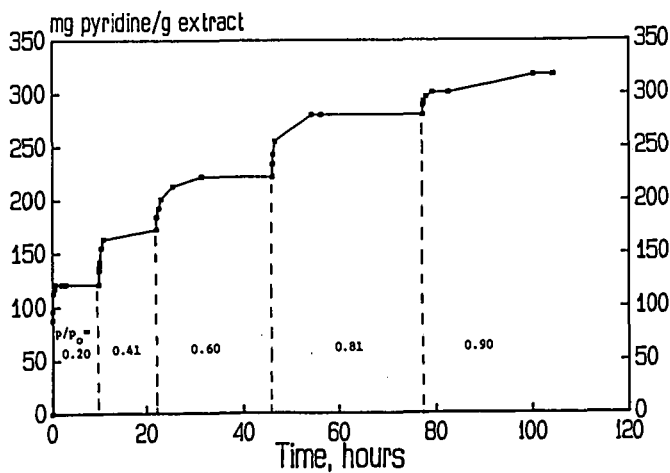


Figure 3. Sorption of Pyridine by O-methylated Pyridine-extract of Illinois No. 6 Coal at 50°C.

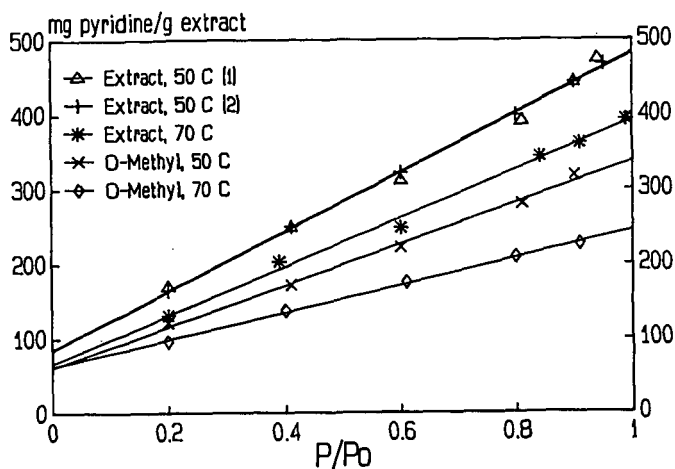


Figure 4. Sorption Isotherms of Pyridine-extracts of Illinois No. 6 Coal.

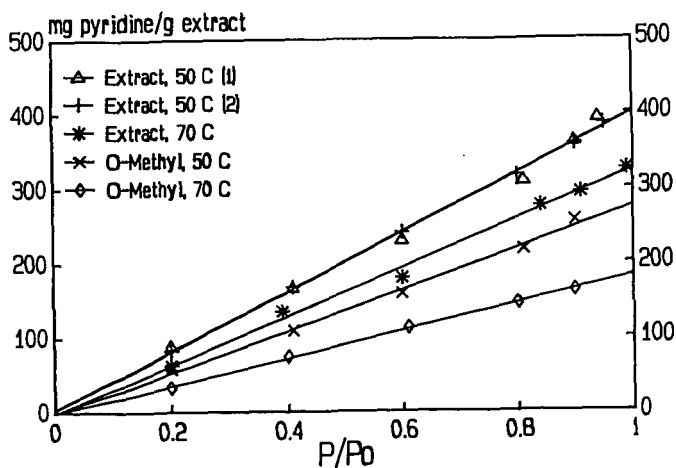


Figure 5. Corrected Sorption Isotherms of Pyridine-extracts of Illinois No. 6 Coal.